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at Alfred University, Alfred, New York

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HYDROGEN-OXYGEN ELECTRODE STUDY

Contract AF 33(657)-7564
Quarterly Technical Progress Report No. 5
15 March 1963

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Project Director

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Alfred University, Alfred, New York

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The work covered by this report was accomplished under Air Force Contract AF 33(657)-7564, but this report is being published and distributed prior to Air Force review. The publication of this report, therefore, does not constitute approval by the Air Force of the findings or conclusions contained herein. It is published for the exchange and stimulation of ideas.

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Summary

Fuel cell electrodes consisting of Clevite Corporation's No. 3 porous nickel (1/16" thick) were found to be very absorbent to potassium hydroxide solutions. Asbestos and Fiberfrax matte were used as electrolyte holders to immobilize the potassium hydroxide. The Fiberfrax was not suitable as it was readily attacked by the potassium hydroxide. The asbestos (1/32" thick) was satisfactory in that it permitted intermittent operation under light loads 1-2 ma/cm^2 over a 2-week period. However, the contact between electrolyte and electrode was not stable due to the drying effect of fuel gases passing over the back of the electrode and the relatively irregular surfaces of the asbestos and the nickel, particularly so when fuel gas flow rates are varied during cell operation. Attempts were made to stabilize the electrolyte-electrode contact by giving the potassium-hydroxide-impregnated asbestos a thin coating of gelled hydroxide.

The metal electrode fuel cell, as described in the Fourth Quarterly Progress Report, was redesigned to overcome a gas leakage and a gas mixing problem experienced when an asbestos electrolyte holder was used.

Clevite No. 3 porous nickel electrodes were soaked overnight in 2.77% $H_2PtCl_6nH_2O$ containing traces of lithia, dried at 140°C, the cathode was oxidized at 450°C in oxygen and the anode was reduced at 300°C in hydrogen. The open-circuit potentials obtained from these electrodes were 0.84 to 0.86 v.

A new electrode holder was developed to facilitate making surface area measurements of porous metal electrodes according to the method of Nelson and Eggertson mentioned in Quarterly Progress Report No. 2.

The procedure for carbonizing polyvinyl powder pressed at 2500 psi was studied and a sample of carbon prepared as a preliminary in the development of a new material for fuel cell electrodes.

Progress Report

As remarked in previous reports, the Clevite Corporation's No. 3 porous nickel electrodes absorb aqueous potassium hydroxide very quickly. The use of a suitable electrolyte holder is therefore essential if a fuel cell constructed with such electrodes is to function for any length of time. During the present reporting period, efforts were concentrated on the problem of finding a suitable electrolyte holder. Fiberfrax matte was tried but it was too readily attacked by the electrolyte. Asbestos was used with some success. Both 1/8" and 1/32" thicknesses were tried. It was possible to incorporate a reference electrode in the thicker material but not so in the case of the thinner material. The rigidity of the asbestos used did not permit intimate enough contact between the electrode and electrolyte holder when the holder was impregnated with only 15% by weight of holder of 30% KOH, a value reported earlier as the amount of KOH which the asbestos would bond or hold loosely. Thus, in order to improve the electrode-electrolyte contact, it was necessary to add more than 30% by weight of holder of KOH solution to the electrolyte holder and when using this amount, in the case of the thicker asbestos, there is a strong tendency for sufficient amounts of KOH to move by capillary attraction from the holder to the electrode to cause drowning. This effect is not so serious in the case of the thinner holder since the total amount of KOH free to move into the electrodes is much less. Thus by soaking a 1/64" asbestos electrolyte holder in 30% KOH, then laying it on a similar matching dry holder and allowing the dry holder to absorb the mobile KOH from the wet holder for a minute or so, the double layered holder so formed was found to contain 80% by weight of 30% KOH. This double layered holder, 1/32" thick, was damp to the touch and was used immediately in a fuel cell assembly between activated porous nickel electrodes. The cell was designed to

minimize evaporation losses from the edge of the asbestos (see Figure 1). Intermittent light loads of 1-2 ma/cm^2 at 0.62 v were drawn from the cell for a two-week period before the cell deteriorated. Thus when fuel cell electrodes are constructed of Clevite Corporation's No. 3 porous nickel (1/16" thickness) and 1/32" thick pure asbestos is used as electrolyte holder, the latter should be impregnated with approximately 80% by weight of holder of 30% potassium hydroxide with reference to the fuel cell design in Figure 1 and gas flow rates of about 10 cc/min through the cell.

A disadvantage of the asbestos electrolyte holder is the relatively poor contact that it makes with the electrode and subsequently an instable electrode-electrolyte contact as a result of formation of water when the cell is under load and the counterbalancing drying effect of dry fuel gases sweeping over the back surfaces of the electrodes. This suggested instability should reflect in fluctuations in cell resistance. An attempt was made to observe such fluctuations with variations of fuel gas flow rates and load variations in a pulsed load using a Keithley 503 Milliohmmeter. However, the interaction of the 60-cycle Kordesch-Marko pulse loading circuit and a 40-cycle circuit in the milliohmmeter gave a beat frequency and needle fluctuation of 20 cycles/second which made it impossible to observe variations in cell resistance with any degree of accuracy. The circuit is being modified and, if possible, the above mentioned variations in cell resistance will be studied.

Evidence of poor contact between electrode and asbestos electrolyte holder was obtained by monitoring the electrode surfaces with moist p-H paper when the cell was disassembled. It was found that either electrode surface in contact with the electrolyte holder was not uniformly alkaline. As a result of these recent tests and previous experience with gelled KOH, it was felt that the effectiveness of an asbestos electrolyte holder could

be increased by incorporating Dow Methocel HG gelling agent in the electrolyte. This should stabilize the electrode-electrolyte contact and increase the capacity of the holder for potassium hydroxide. This will be tried during the next reporting period. Some work has been performed on the technique of applying the gel.

In order to learn more about the potential uses of gelled electrolyte, i.e., not in combination with another electrolyte holder, experiments were carried out to establish the best techniques for preparing a gelled electrolyte. Slow addition of Dow Methocel HG to hot 15% KOH with slow mechanical agitation and the beaker containing the KOH resting in an ultrasonic bath, yielded a smooth gel.

Gels prepared in the above manner were used between activated graphite electrodes (Great Lakes Carbon Company's H204). Twice fuel cells assembled with these components gave 0.92 v under light load even though on each attempt the anode was fractured during cell assembly. Further, the electrolyte penetration into the electrode was not more than one millimeter at the cracks and 0.5 millimeter on unbroken surfaces. The fact that these cells operated for several days under the condition mentioned indicates a safety feature of a gelled electrolyte; namely, prevention of mixing of fuel gases and subsequent explosion or heating hazards. This would apply in the case of minor failure, a small crack for example. In the case of a major failure such as shattering, the gel will dry, shrink and permit mixing of fuel gases in a shorter time.

The gelled potassium hydroxide prepared with Methocel HG, hydroxypropyl methyl cellulose, did not show any signs of breaking down within a two month-period, whereas gels prepared with Natrosol, hydroxyethyl cellulose gelling agent, showed signs of decomposition within a week. Of the gelling agents investigated to date, the hydroxypropyl methylcellulose has given best results.

As mentioned above, the metal electrode fuel cell described in the Quarterly Progress Report No. 4 has been redesigned. This was done to overcome gas leakage around the ends of the electrodes and also to permit the use of a reference electrode when thin (1/32" thick) asbestos was used as an electrolyte holder. The new design is shown in Figure 2.

The activation of No. 3 Clevite porous nickel electrodes was improved by soaking the electrodes in 2.77% $H_2PtCl_6nH_2O$ overnight rather than for a few minutes as was done previously and by incorporating trace quantities of lithia. The electrodes were then dried in vacuum followed by heating in vacuum to 400°C overnight, and cooled in vacuum. The cathode was then heated in oxygen to 450°C and cooled in oxygen. The anode was heated in hydrogen for about 1 hour at 300°C and cooled in hydrogen. Maximum open circuit potential was 0.86 v. While the potential was probably a combined potential including oxidation reduction reactions other than those of the ideal hydrogen-oxygen fuel cell, it was felt that certain refinements must be made in procedure for activating these electrodes. Maximum current density obtained from the cell just mentioned was 1-2 ma/cm^2 at 0.62 v over a two-week period.

While on pulse load a fluctuation in potential was observed. The frequency of this fluctuation could be varied from about 30 minutes to several hours by varying rates of fuel gases. The potential buildup in this cycle was very fast and the decay time very slow. The exact cause of this phenomenon has not so far been determined.

The electrode holder described in Quarterly Progress Report No. 2 for use with the Nelson and Eggertson method for surface area measurements was not suitable for thinner, larger diameter metal electrodes. A new holder was designed which is more versatile in that it will take electrodes up to 3" diameter and any practical thickness. Measurements made to date

with this holder have been satisfactory and final tests and slight improvements in design are being carried out at present.

As mentioned in earlier reports, it was hoped on this project to make a test fuel cell electrode material after the method of Gray in which a catalyst is integrally mixed with an organic polymer powder and pressed in a metal mesh supporting screen and the whole then carbonized to yield a very pure carbon with catalyst throughout. Accordingly, a carbonization furnace and auxiliary equipment were set up and four experiments have been performed to establish proper carbonization procedure. One of the experiments yielded a porous high strength carbon. It is hoped that experiments can be performed with such a material to establish the effect of impurity species on fuel cell performance.

Figure 1

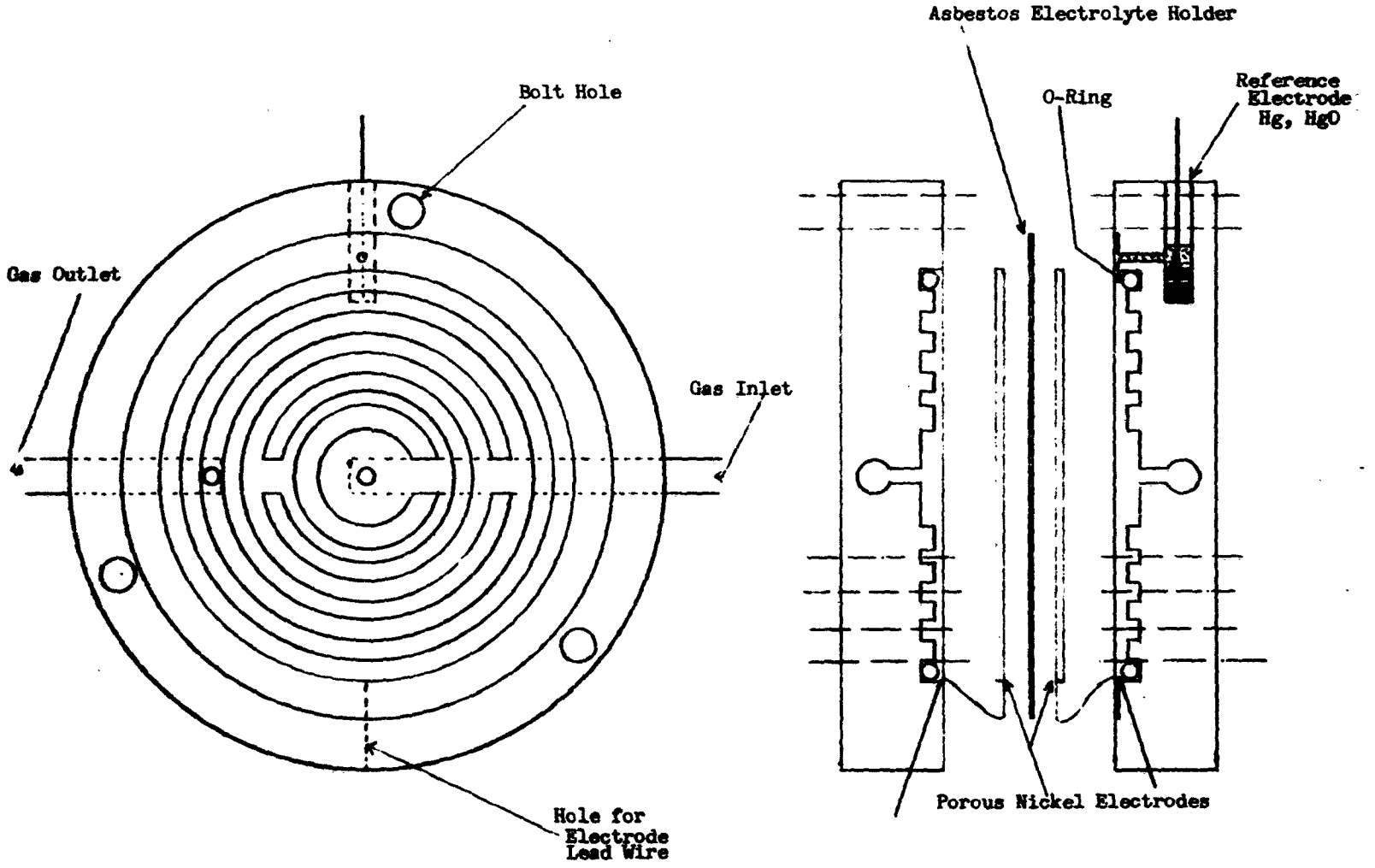
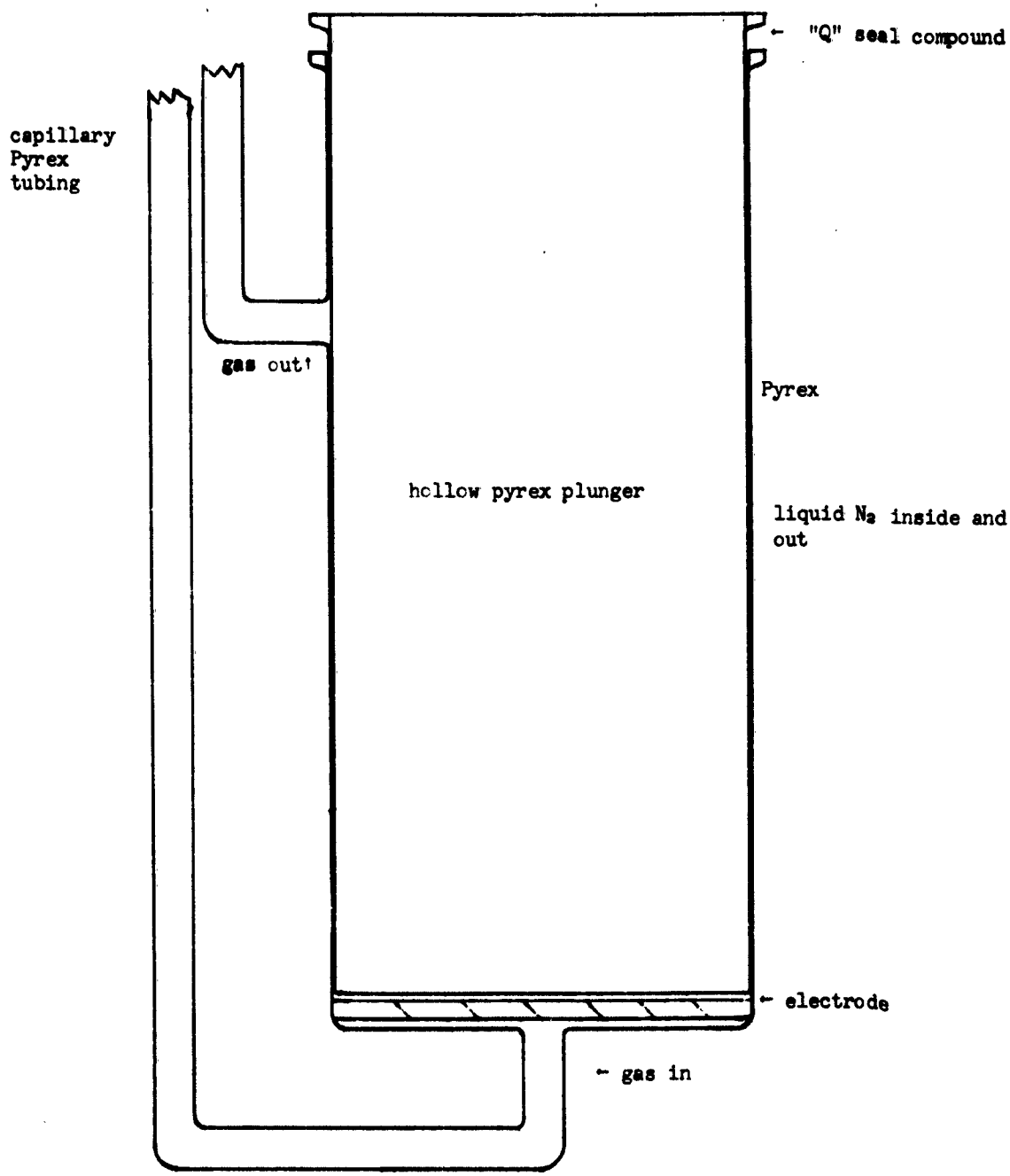

Asbestos Electrolyte Holder
Bolt Hole
O-Ring
Reference Electrode Hg, HgO
Gas Outlet
Gas Inlet
Hole for Electrode Lead Wire
Porous Nickel Electrodes

Figure 2



Electrolyte Holder for Surface Area Measurement

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